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Sulfur addition to aldimines: thioamides, not thiaziridines as products; revision of an old report

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Dedicated to *Professor Rolf Huisgen*, Ludwig-Maximilians-Universität München, Germany, on the occasion of his 85th birthday

The reaction of 4-(phenylimino)butan-2-ol with ammonium polysulfide in refluxing EtOH yields 3-hydroxy-*N*-phenylbutanethioamide as the only isolated product. The structure has been established by single crystal X-ray diffraction. Treatment of *N*-benzylidenamines with ammonium polysulfide has proven a general method for the preparation of thiobenzamides.

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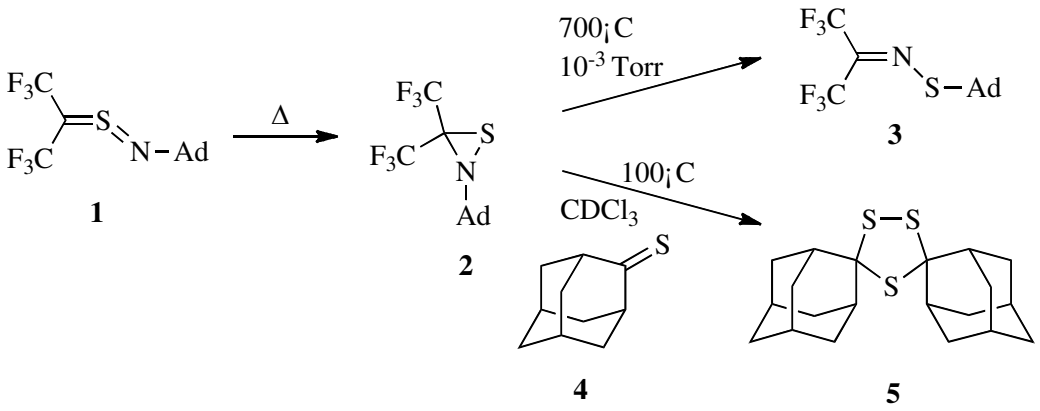
Key words: Azomethines; Sulfur transfer; Thiaziridines; Thioamides

Introduction

Sulfur-containing saturated three-membered heterocycles are compounds with significant importance not only in organic synthesis but also for theoretical and spectroscopic studies.[1-6] Of these, only thiiranes are well known, fully characterized and frequently used materials.[1] Among the derivatives with two heteroatoms in the three-membered ring, some dithiiranes have been prepared, isolated, and characterized recently,[7] whereas oxathiiranes are sometimes involved as intermediates in desulfurization processes of sulfines (thiocarbonyl *S*-oxides).[8] Similarly, thiaziridines have been postulated as intermediates in transformations of thiocarbonyl *S*-imides into imines.[9-11]

In our recent studies on reactions of thiocarbonyl compounds with organic azides, thiaziridines were proposed as key intermediates in the sulfur-transfer process leading to the *in situ* formation of thiocarbonyl *S*-sulfides, which further react to give 1,2,4-trithiolanes.[12] As a possible precursor of a thiaziridine, the stable thiocarbonyl *S*-imide **1** was thermolyzed under FVP-conditions. The only product isolated was the rearranged compound **3**[13] (Scheme 1). Thiaziridine **2** was postulated as the intermediate, which in the gas-phase undergoes a conversion to **3** without elimination of sulfur. On the other hand, heating of **1** in $CDCl_3$ in the presence of adamantanethione (**4**) led to the known 1,2,4-trithiolane **5**.[14,15] In accordance with the proposed sulfur-transfer reactions,[12]

thiaziridine **2** is believed to act as the S-donor, which transfers **4** into the corresponding thiocarbonyl *S*-sulfide. The latter undergoes a [3+2] cycloaddition with **4** to give **5**.

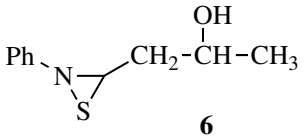


Scheme 1

To the best of our knowledge, there exist only two reports, in which isolated reaction products are formulated as thiaziridines.[16,17]† In one of them, published in 1896, treatment of 4-(phenylimino)butan-2-ol ('Aldolanilin') with ammonium polysulfide ('Schwefelammon')§ in EtOH was described as a method for the preparation of thiaziridine **6**.[16] More then 70 years later, thiaziridine structures of type **7** were included into the Beilstein Database as patented benzodiazepine derivatives.[17]

† Thiaziridine-1,1-dioxides with bulky substituents are known as isolable compounds.[2][18]

§ 'Schwefelammon' means literally NH_4HS and $(NH_4)_2S$; the sulfidation reactions described[16] leave no doubt, however, that the rather unstable compound NH_4HS had become oxidized to the polysulfide, at least partially, before or during the reaction, fortuitously or on purpose.



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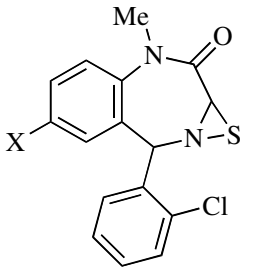

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Due to our current interest in reactions involving thiaziridines as intermediates, we decided to repeat the experiment reported by *v. Miller* and *Plöchl*[16] with the aim of proving unequivocally the structure of the crystalline reaction product, whose identity so far rests on its elemental composition only.

Results and Discussion

The imine **8**[19] is an unstable compound (*cf.* ref.[16]) and was used as starting material for the reaction with freshly prepared ammonium polysulfide, $(NH_4)_2S_x$, without further purification. Heating of a mixture of **8** and excess $(NH_4)_2S_x$ in EtOH under reflux for 5 min led to an orange viscous oil, which was purified by column chromatography. Besides elemental sulfur, only one organic product was isolated and recrystallized from petroleum ether/Et_2O to give almost colorless crystals. The melting point and elemental analysis were in accordance with the data reported by *v. Miller* and *Plöchl*.[16] In the ^{1}H NMR spectrum ($CDCl_3$), two broad signals at 3.16 and 9.72 ppm for OH and NH showed that the structure differs from **6**. The ^{13}C NMR spectrum revealed two sets of signals (ratio ca. 10:1) corresponding to the structures of two rotamers of thioamide **9**‡ with the characteristic C=S resonance at 202.4 ppm. Finally, the structure of **9** was established by

‡ The doubling of the signals results from the presence of two rotamers (*cf.* ref.[20]).

single crystal X-ray analysis (Figure). Thus, the substance described in ref.[16] as thiaziridine **6** is actually the β-hydroxythioamide **9**. This class of compounds has been only rarely described.[22]

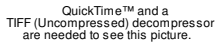
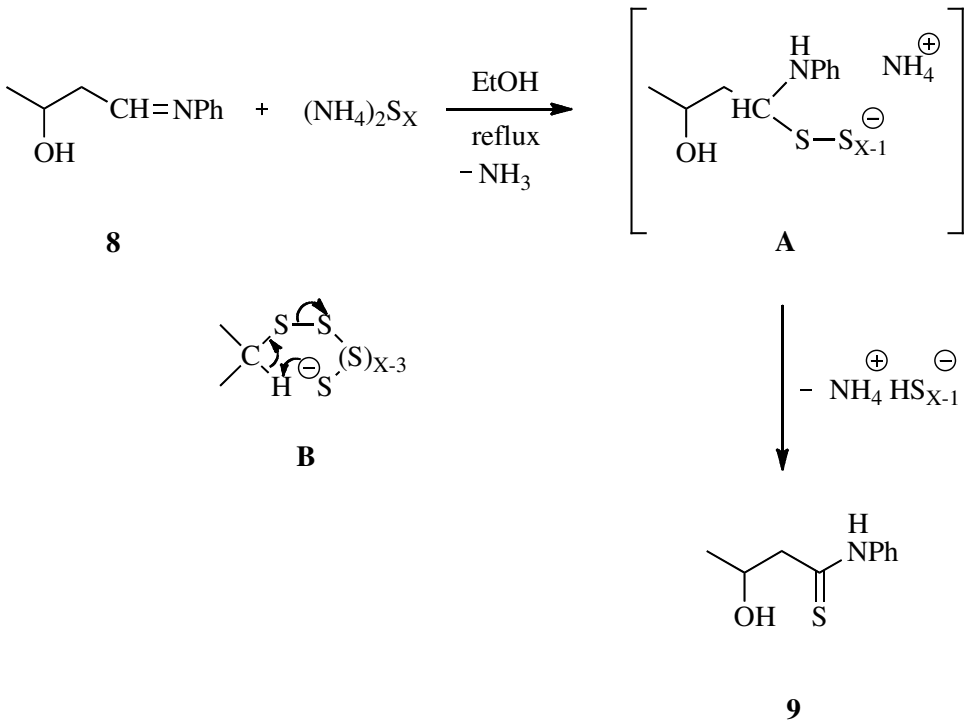


Figure. Displacement ellipsoid plot (50% probability) [21] of one of the two symmetrically independent molecules of **9**

The asymmetric unit contains two molecules of very similar conformation. In addition to intramolecular hydrogen bonds between the sulfur and oxygen atom (distance O....S 3.047(4) and 3.062(4)Å, resp.), intermolecular hydrogen bonds between NH and the O-atom link neighboring molecules to chains along the [100] direction.

A possible explanation of the reaction pathway leading to **9** is shown in Scheme 2. The first step is a nucleophilic addition of the polysulfide anion to the imino group of **8** to

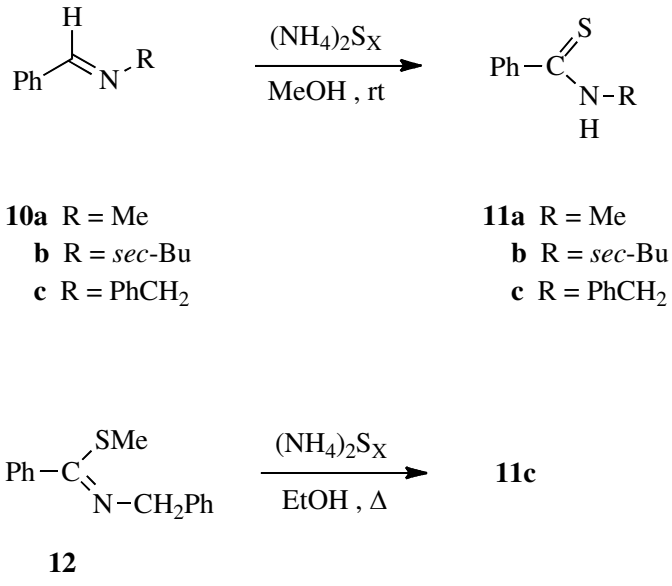
give an ion pair **A**. Then, the thioamide **9** is formed by elimination of ammonium hydropolysulfide. For this elimination, a cyclic transition state of type **B** is likely.



Scheme 2

It has been shown that differently substituted aldimines can be converted into thioamides by treatment with elemental sulfur. In all cases reported, high temperature (100-260 °C) is required to perform the reaction.[23] In some cases, mixtures of sulfur and H_2S were applied without heating.[24] However, reports on reactions of imines with $(NH_4)_2S_x$ aimed at the preparation of thioamides are not known. Therefore, reactions of aldimines **10** with ammonium polysulfide were carried out in our laboratories. The transformations occurred smoothly in MeOH already at room temperature (1 h) to give the expected thioamides **11**,

albeit in moderate yields of less than 50% (Scheme 3). On the other hand, this protocol was inefficient in the case of *N*-(benzyliden)aniline (**10d**, R = Ph).

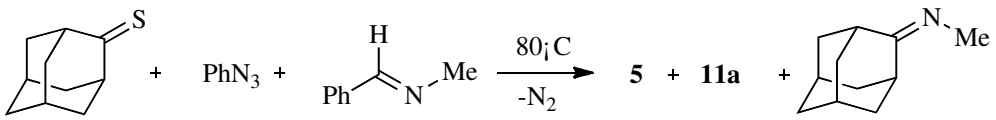


Scheme 3

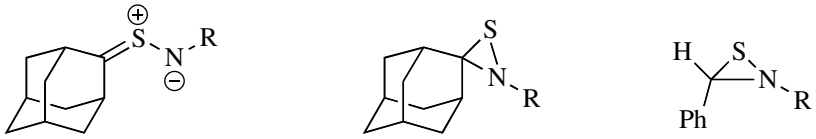
As an additional experiment, thiobenzimidate **12** was treated with $(NH_4)_2S_x$ in boiling EtOH. The reaction proceeded by formal elimination of MeSH, and thioamide **11c** was isolated in 45% yield. A convincing mechanism for this reaction cannot be presented yet.

The formation of 1,2,4-trithiolanes of type **5** in the reactions of thioketones with organic azides was rationalized by sulfur-transfer processes, which are initiated by transient thiocarbonyl *S*-imides **C** (Scheme 4). Ring closure leads to unstable thiaziridine derivatives of type **D**, which act as sulfur donor.[12] With the aim of examining the ability of aldimines as sulfur acceptors in this system, a three-component reaction using **4**, phenyl azide, and **10a** was carried out at 80 °C. The ^{1}H NMR analysis of the crude

product indicated the presence of **11a**, which was subsequently isolated after chromatographic workup along with comparable amounts of **5** (Scheme 4). As mentioned in our previous report,[12] the isolation of the imine **13** is not possible under these conditions. The formation of **11a** is a strong evidence that aldimines **10** are reactive sulfur acceptors, and thiaziridines of type **E**, i.e. derivatives of aldimines, are likely intermediates that undergo an intramolecular stabilization via ring opening and H-shift. In contrast, thiaziridines of type **D**, derived from ketimines, are subjected to a sulfur extrusion. Similar rearrangements of oxaziridines, generated thermally or photochemically from aldonitrones or heterocyclic *N*-oxides or obtained by oxidation of the imine precursors, leading to carboxamides are well documented.[25]



4 **10a** **13**



C **D** **E**

Scheme 4

Conclusions

Our study shows that the product of the reaction of **8** and $(NH_4)_2S_x$ described in ref.[16] is neither the thiaziridine **6** nor the isomeric thionitrone but the thioamide **9**. As proposed in Scheme 2, the formation of **9** does not require a thiaziridine as an intermediate. However, the intermediacy of such species cannot be excluded in the reactions with elemental sulfur, in analogy to oxidation of imines leading to oxaziridines.[26] In the light of the presented results, the thiaziridine structures of type **7** are also questionable.

The synthesis of thioamides from easily available aldimines and $(NH_4)_2S_x$ supplements known procedures for the preparation of this important class of organic compounds (*cf.* ref.[27]). In spite of the fact that the formation of thioamides in three-component reactions (Scheme 4) is not important from the preparative point of view, this is the first evidence that aldimines are sulfur acceptors, which efficiently compete with thioketones.

Experimental

1. General. Melting points were determined in capillaries on a Melt-Temp II apparatus (*Aldrich*) and are not corrected. IR spectra were registered with a NEXUS FT-IR spectrophotometer (in KBr). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Tesla BS567A (80 and 20 MHz, resp.) or Varian Gemini 200-BB (^{1}H, 200 MHz) instrument. The multiplicity of the ^{13}C signals was deduced from DEPT spectra. Elemental analyses were performed by the Microanalytical Laboratory of the *Polish Academy of Sciences* in Lodz.

2. Starting materials. *3-Hydroxybutanal* was prepared from acetaldehyde in the presence of a 10% aqueous NaOH solution according to a known procedure.[28] The preparation of the corresponding phenylimine **8** was carried out following the method described by *v. Miller* and *Plöchl*.[16] The crude product, which precipitated from Et_2O solution after addition of small amounts of hexane, was separated as a semi-solid orange material and was used for the reaction with $(NH_4)_2S_x$ without further purification. Attempted distillation of **8** *in vacuo* as well as column chromatography led to complete decomposition. *(3-Hydroxybutyliden)aniline* (**8**): Almost quantitative yield (crude material, unstable). ^{1}H NMR (80 MHz): 0.58-2.17 (*m*, 6 H); 4.83 (*d*, OH); 6.33-6.93 (*m*, 3 arom. H); 6.97-7.32 (*m*, 2 arom. H); 7.33 (*s*, CH=N). N-*Benzylidenemethylamine* (**10a**),[29] N-*benzylidene(1-methylpropyl)amine* (**10b**),[30] and N-*benzylidenebenzylamine* (**10c**)[31] were prepared according to known procedures from the corresponding amine and benzaldehyde. Pellets of KOH were added to improve separation of the organic and aqueous layers. Pure products were obtained by distillation *in vacuo*. N-*Benzyl*-S-*methylthiobenzimidate* (**12**) was prepared from methyl dithiobenzoate and benzylazide according to ref.[32] *Ammonium polysulfide*, $(NH_4)_2S_x$, was obtained from NH_3, H_2S, and elemental sulfur following the protocol in ref.[33] The red-orange crystals were stored in EtOH solution in the refrigerator. Immediately before use, an aliquot was filtered and washed with Et_2O.

3. Reaction of 8 with $(NH_4)_2S_x$. A solution of **8** (2.02 g, 12 mmol) in abs. EtOH (5 ml) was treated with an excess of freshly filtered $(NH_4)_2S_x$ (2.36 g), the mixture was heated to reflux for 5 min, and EtOH was evaporated subsequently. The solid residue was treated

with Et_2O (20 ml) and elemental sulfur was separated by filtration. The clear Et_2O solution was diluted with small portions of petroleum ether until a colorless precipitate appeared. The solid was filtered and the solution was stored in the refrigerator. After several h, a crystalline product was formed and filtered. The mother liquor was again stored in the refrigerator to give another crop of crystals which was combined with the first portion. Analytically pure **9** was obtained after recrystallization from MeOH.

3-Hydroxy-N-*phenylbutanethioamide* (**9**). Yield: 435 mg (18%). Mp. 92-93 °C (ref.[16]: 92 °C). IR (KBr): 3000-2800*vs* (br., OH), 1597*m*, 1559*m*, 1497*s*, 1414*vs* (br.), 1311*s*, 1207*s*, 1146*s*, 767*s*, 715*vs*, 691*s*. ^{1}H NMR (200 MHz; major rotamer (85%)): 1.32 (*d*, *J* = 6.3, Me); 2.87 (*dd*, *J* = 15.1, 8.5, H_B of CH_2); 3.03 (*dd*, *J* = 15.1, 2.6, H_A of CH_2); 3.16 (broad *d*, *J* = ca. 3.3, OH); 4.00-4.55 (*m*, CH); 7.25-7.75 (*m*, 5 arom. H); 9.72 (broad *s*, NH). The ratio of the rotamers (85:15) was estimated from the intensities of the Me signals at 1.32 (major) and 1.55 ppm (minor). ^{13}C NMR: 23.0 (*q*, Me); 55.5 (*t*, CH_2); 67.1 (*d*, CH); 124.2, 127.2, 129.2 (3*d*, 5 arom. CH); 139.0 (*s*, arom. C); 202.4 (*s*, C=S). Signals of the minor rotamer (15%) were found at 22.3, 48.0, 66.4, 126.0, 128.7, 130.1, 137.8, and 205.0. Anal. calc. for $C_{10}H_{13}NOS$ (195.28): C 61.51, H 6.71, N 7.17, S 16.42; found: C 61.30, H 6.89, N 7.24, S 16.50 (ref.[16]: found: C 61.52, H 6.92, N 7.32, S 16.36).

In another experiment, the Et_2O solution obtained after separation of the colored, oily by-products was evaporated and the residue was purified by column chromatography (SiO_2) using petroleum ether with increasing amounts of dichloromethane as the eluent. Crude **9** was obtained as the main fraction (660 mg, 27%) and purified by crystallization from petroleum ether containing small amounts of dichloromethane.

4. Reactions of imines 10a-c with $(NH_4)_2S_x$. *General procedure*. A mixture of the imine **10a**-**c** (10 mmol) and freshly filtered $(NH_4)_2S_x$ (2.0 g) in MeOH (10 ml) was stirred at room temperature. After 1 h, MeOH was evaporated and the semi-solid residue was triturated with 20 ml of Et_2O. The precipitated sulfur was filtered off, and after evaporation of the solvent, the crude thioamide **11a**-**c** was crystallized from MeOH.

N-*Methylthiobenzamide* (**11a**). Yield: 634 mg (42%). Mp. 75-76 °C (ref. [34]: 77-79 °C). ^{13}C NMR: 200.4 (*s*, C=S) (ref.[34]: 200.0).

N-*(1-Methylpropyl)thiobenzamide* (**11b**). Yield: 929 mg (48%). Mp. 42-43.5 °C (ref. [35]: 47-48 °C). ^{13}C NMR: 10.4, 18.9 (2 *q*, 2 Me); 28.7 (*t*, CH_2); 53.6 (*d*, CH); 127.0, 128.6, 131.1 (3 *d*, 5 arom. CH); 142.6 (*s*, 1 arom. C); 198.6 (*s*, C=S).

N-*Benzylthiobenzamide* (**11c**).[¶] Yield: 976 mg (43%). Mp. 87-88 °C (ref. [35]: 85-87 °C). ^{13}C NMR: 199.7 (*s*, C=S) (ref.[34]: 199.3).

5. Three-component reaction with *N*-benzylidenemethylamine (10a), adamantanethione (4), and phenyl azide. Thioketone **4** (166 mg, 1 mmol) and **10a** (238 mg, 2 mmol) were dissolved in 0.5 ml of phenyl azide, and the magnetically stirred orange solution was heated at 80 °C. The evolution of nitrogen was monitored by means of a gas burette connected with the reaction flask. When the gas evolution ceased, the crude mixture was analysed by ^{1}H NMR and the ratio of *N*-methylthiobenzamide (**11a**) and *N*-benzylidenemethylamine (**10a**) was determined to be ca. 1:3. The volatile components were removed by distillation in an oil pump vacuum and the residual thick

[¶] Compound **11c** was also obtained in 45% yield after treatment of *methyl* N-*benzylthiobenzimidate*[36] with $(NH_4)_2S_x$. The reaction was carried out in refluxing EtOH; reaction time 1 h.

oil was separated on preparative plates coated with SiO_2 (eluent dichloromethane). *N*-Methylthiobenzamide (**11a**) was recrystallized frome benzene. Yield: 40 mg (26%). ^{1}H NMR and IR spectra were identical with an original sample. Trithiolane **5** was isolated as a less polar fraction and was recrystallized from MeOH. Yield: 106 mg (29%). ^{1}H NMR and IR spectra were identical with an original sample (cf. ref. [12]).

6. X-Ray crystal-structure determination of 9 (see Table 1 and Fig. 1).[#] A crystal was mounted on a glass fiber for geometry and intensity data collection with a Bruker SMART Apex CCD area detector on a D8 goniometer. Preliminary lattice parameters and orientation matrices were obtained from three sets of frames. All data were collected using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) with the ω scan method[37] and processed with the SAINT+ program.[38] The structure was solved by direct methods and refined using SHELXTL.[39] Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms on carbons were placed in idealized positions (C-H = 0.98 Å) and included as riding with U_{iso}(H) = 1.3 U_{eq}(non-H). Hydrogen atoms bonded to nitrogen or sulfur atoms were located from difference Fourier maps and refined freely and isotropically. Anomalous dispersion effects were sufficient to determine the polarity of the individual crystal in the non-centrosymmetric space group $Pna2_1$; an enantiomorph polarity parameter[40] of 0.01(16) was obtained.

[#] CCDC-247195 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* **www.ccdc.cam.ac.uk/conts/retrieving.html** (or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data, data collection parameters and refinement results are listed in Table 1, and a view of the molecule is shown in Fig. 1.

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REFERENCES

[1] a) A. W. Fokin, A. F. Kolomiejc. *Khimija Thiiranov*, Nauka, Moskva (1978); b) W. Ando, N. Choi, N. Tokitoh. In *Comprehensive Heterocyclic Chemistry II*, A. R. Katritzky, C. W. Rees and E. F. V. Scriven (Eds.), Vol. 1A, A. Padwa (Ed.), pp. 173-240, Pergamon, Oxford (1996).

[2] U. Zoller. *Sulfur Reports*, **20**, 173-195 (1997); U. Zoller. In *Comprehensive Heterocyclic Chemistry II*, A. R. Katritzky, C. W. Rees, E. F. V. Scriven (Eds.), Vol. 1A, A. Padwa (Ed.), pp. 415-428, Pergamon, Oxford (1996).

[3] U. Zoller. In *The Chemistry of Heterocyclic Compounds*, Vol. 42*, Small-Ring Heterocycles*, Part 1, A. Hassner (Ed.), pp. 333-630, J. Wiley & Sons, New York (1983).

[4] Ch. Larksarp, O. Sellier, H. Alper. *J. Org. Chem.*, **66**, 3502-3506 (2001).

[5] G. Mloston, J. Romanski, H. P. Reisenauer, G. Maier. *Angew. Chem. Int. Ed.,* **40**, 393-396 (2001).

[6] a) W. Sander, A. Kirschfeld. *Adv. Strain Org. Chem.*, **4**, 1-80 (1995); b) Y. Steudel, R. Steudel, M. W. Wong. *Chem. Eur. J.*, **8**, 217-228 (2002).

[7] J. Nakayama, A. Ishii. *Adv. Heterocycl. Chem.,* **77**, 221-284 (2000); A. Ishii, T. Omata, K. Umezawa, J. Nakayama. *Bull. Chem. Soc. Jpn.,* **73**, 729-737 (2000), and refs. cited therein.

[8] D. Chevrie, P. Metzner. *Tetrahedron Lett.,* **39**, 8983-8986 (1998).

[9] L. N. Markovskii, V. M. Timoshenko, Yu. G. Shermolovich. *Zh. Org. Khim.*, **31**, 161-178 (1995).

[10] J. Fabian, G. Mloston. *Pol. J. Chem.,* **73**, 669-681 (1999).

[11] S. Pekcan, H. Heimgartner. *Helv. Chim. Acta,* **71**, 1673-1680 (1988).

[12] G. Mloston, H. Heimgartner. *Helv. Chim. Acta,* **78**, 1298-1310 (1995); G. Mloston, J. Romanski, H. Heimgartner. *Pol. J. Chem.*, **70**, 437-445 (1996); G. Mloston, J. Romanski, A. Linden, H. Heimgartner. *Pol. J. Chem.*, **70**, 880-890 (1996).

[13] G. Mloston, S. Lesniak, A. Linden, H. W. Roesky. *Tetrahedron*, **56**, 4231-4238 (2000).

[14] G. Mloston, M. Celeda, H. W. Roesky, E. Parisini, J.-T. Ahlemann. *Eur. J. Org. Chem.*, 459-465 (1998).

[15] A. Linden, C. Fu, A. Majchrzak, G. Mloston, H. Heimgartner. *Acta Cryst.*, *Sect. C*, **58**, o231-o234 (2002).

[16] W. v. Miller, J. Plöchl. *Ber. Dtsch. Chem. Ges.*, **29**, 59-61 (1896).

[17] Beilstein Database BS0402AB, ref. No. 5-27.

[18] H. Quast, F. Kees. *Angew. Chem. Int. Ed.*, **13**, 742-743 (1974); H. Quast, F. Kees. *Chem. Ber.*, **114**, 774-786 (1981).

[19] G. Münch in: W. v. Miller, J. Plöchl. *Ber. Dtsch. Chem. Ges.*, **27**, 1281-1296 (1894), pages 1292 and 1293.

[20] a) W. Bauer, K. Kühlein. In *Houben-Weyl, Methoden der Organischen Chemie*, Vol. E5, J. Falbe (Ed.), Georg Thieme Verlag, Stuttgart, pp. 1218-1279 (1985); b) G. I. Sarapulova, G. K. Balakhchi, L. L. Dmitrieva, N. A. Nedolya. *Russ. J. Org. Chem.*, **37**, 1714-1718 (2001).

[21] A. L. Spek. *Acta Cryst., Sect. A,* **46**, C-34 (1990).

[22] H. Takahata, K. Yamazaki, T. Takamatsu, T. Yamazaki, T. Momose. *J. Org. Chem.*, **55**, 3947-3950 (1990); M. Cinquini, A. Manfredi, H. Molinari, A. Restelli. *Tetrahedron*, **41**, 4929-4936 (1985); J. Sawlewicz, M. Grzybowski. *Acta Pol. Pharm.*, **35**, 273-280 (1978); for N-unsubstituted analogues: F. L. Austin, C. A. Gent. *Chem. Commun.*, 71-72 (1967); for N,N-disubstituted analogues: R. E. Ireland, F. R. Brown. *J. Org. Chem.*, **45**, 1868-1880 (1980); M. Cinquini, A. Manfrdi, H. Molinari, A. Restelli. *Tetrahedron*, **41**, 4949-4936; P. Berlin, B. Lelong. *Tetrahedron*, **53**, 17253-17246 (1997).

[23] K. Kindler. *Liebigs Ann. Chem.*, **431**, 187-230 (1923); B. Böttcher, F. Bauer. *Liebigs Ann. Chem.*, **568**, 218-225 (1950); M. Haddad, F. Dahan, J.-P. Legros, L. Lopez, M. T. Boisdon, J. Barrans. *J. Chem. Soc., Perkin Trans. 2*, 671-678 (1992).

[24] R. Wegler, E. Kühle, W. Schäfer. *Angew. Chem.*, **70**, 351-367 (1958).

[25] G. R. Delpierre, M. Lamchen. *Quart. Rev.*, 329-349 (1965).

[26] F. A. Davis, A. C. Sheppard. *Tetrahedron*, **45**, 5703-5742 (1989).

[27] K. E. DeBruin, E. E. Boros. *J. Org. Chem.*, **55**, 6091-6098 (1990).

[28] L. P. Kyriakides. *J. Am. Chem. Soc.*, **36**, 530-537 (1914).

[29] W. K. Anderson, A. S. Milowsky. *J. Med. Chem.*, **11**, 2241-2249 (1986).

[30] R. E. Lutz, P. S. Bailey, R. J. Rowlett, Jr., J. W. Wilson, III, R. K. Allison, M. T. Clark, N. H. Leake, R. H. Jordan, R. J. Keller, III, K. C. Nicodemus. *J. Org. Chem.*, **12**, 760-766 (1947).

[31] R. G. Cooks, P. Sykes. *J. Chem. Soc. C*, 2864-2871 (1968).

[32] J. Supniewski. *Preparatyka Nieorganiczna*, PWN, Warszawa, pp. 233-234 (1958).

[33] R. Mukherjee, M.M. Moriarty. *Tetrahedron*, **32**, 661-664 (1976).

[34] A. B. Charette, M. Grenon. *J. Org. Chem.*, **68**, 5792-5794 (2003).

[35] M. R. Kanyonyo, A. Gozzo, D. M. Lambert, D. Lesieur, J. H. Poupaert. *Bull. Soc. Chim. Belg.*, **106**, 39-45 (1997).

[36] G. Mloston, J. Romanski, H. Heimgartner. *Pol. J. Chem.*, **75**, 975-928 (2001).

[37] SMART (version 5.624). *Program for Bruker CCD X-ray Diffractometer Control*, Bruker AXS Inc., Madison, WI (2000).

[38] SAINT+ (version 6.02). *Program for Reduction of Data Collected on Bruker CCD Area Detector Diffractometer*, Bruker AXS Inc., Madison, WI (1999).

[39] G. M. Sheldrick, SHELXTL, version 5.1. *Program Package for Structure Solution and Refinement*, Bruker Analytical X-ray Systems, Inc., Madison, WI (1998).

[40] H. D. Flack. *Acta Cryst., Sect. A*, **39**, 876-881 (1983).

Table 1: Crystal data, data collection parameters, and convergence results for **9**

	9
Empirical formula	$C_{10}H_{13}NOS$
Formula weight	195.27
Crystal system	orthorhombic
Space group	$Pna2_1$
Radiation (λ [Å])	Mo-$K\alpha$ (0.71073)
a [Å]	11.1385(13)
b [Å]	11.9536(14)
c [Å]	15.6527(19)
V [Å^3]	2084.1(4)
Z	8
d_{calcd} [g/cm^3]	1.245
$F(000)$	832
μ [mm^{-1}]	0.271
θ range [deg]	2.1–28.4
Completeness of data	0.997
Temperature [K]	293
Crystal size [mm]	0.63 × 0.13 × 0.10
Reflections collected	26575
R_{int}	0.103
Reflections unique	2702
Refls unique observed $I > 2\sigma(I)$	1368
Variables	251
R_1 (obs. data, all data)	0.0574, 0.1210
wR_2 (obs. data, all data,)	0.1331, 0.1552

GOF	0.896
Max. resd. density [e/Å^3]	+0.353 / -0.183